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ANALYSIS OF SHEET-GLASS PRODUCTION IN LARGE-TONNAGE GLASSMAKING FURNACES

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The process of making float-glass in large-tonnage glassmaking furnaces is analyzed. The optimal values of the rate and duration of melting and cooling of the molten glass are determined. It is shown that the melting time of the glass is 48 – 72 h and depends on the content of the cullet in the batch. The glass melt remains chemically and structurally uniform with cooling rates 10 – 12 K/h and cooling times 20 – 24 h, which yields glass of optimal quality.

Key words: float-glass, melting rate, glass cooling stages, glass-melt uniformity, fining, de-polymerization, nanostructure.

Optical quality, heat-polished, sheet glass is an important technical material. Up to 70% of the total production of this glass goes to industrial reprocessing for the manufacture of glass articles of different kinds, such as solar cells (photoelectric modules), glass with different kinds of coatings and other high-tech products. This dictates the need for ensuring high glass quality and stability.

In recent years there have been many technological and technical advances, including domestic, that have determined the progressive development in Russia of float, container and other types of glass [1 – 4]. Developers have focused their attention mainly on increasing glass quality, the key to which is chemical and thermal uniformity of the molten glass used for forming glass ribbon with different nominal parameters. The complexity of the glass melting process lies in the fact that the molten glass fined and homogenized at temperatures of the order of 1460 – 1500°C must be efficiently cooled by 250 – 300°C in a relatively short time to the next stage of formation, while preserving the chemical and thermal uniformity of the glass and viscosity of the order of $10^2 – 10^{2.5}$ Pa · sec suitable for forming [5].

In this respect the most important elements of the sheet-glass production process are the purity and stability of the chemical composition of the raw materials, the batching accuracy and mixing quality and the melting temperatures and times.

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The process of making silicate glasses includes the following stages:

– silicate and glass formation reactions with sodium, calcium and magnesium alkali silicates and silica dissolving in the melt in the temperature interval 700 – 1000°C;

– polymorphic transformations and de-polymerization of the silica in the temperature interval 1000 – 1500°C, ensuring the formation of a structurally uniform glass melt;

– fining and homogenization of the molten glass at temperatures of the order of 1500°C;

– cooling of the molten glass to 1150°C and feeding a continuous glass ribbon into the glass formation stage.

The use of modern technological lines with large-tonnage glassmaking furnaces with capacity to 100 tons/day, new glass-forming equipment and reliable control systems to control the technological processes at all stages of production has made it possible to increase the output of high-quality product to 90 – 92%. The specific energy consumption of glassmaking furnaces and the emission of the ecologically harmful oxides CO_2 and NO_x have decreased by 50% over the last 20 years. However, the chemical nonuniformity of the glass remains one of its main drawbacks.

The chemical uniformity of the glass is determined by the homogenizing capacity of the glassmaking furnace and by the melting time and temperature. It should be kept in mind that just as the specific extraction from 1 m^2 of the melting part of the furnace the productivity of air-gas, gas-oxygen and gas-electric as well as electric glassmaking furnaces is different. This raises the question of how long the molten glass can remain in the furnace without losing chemically uniformity as a result of natural structuring processes

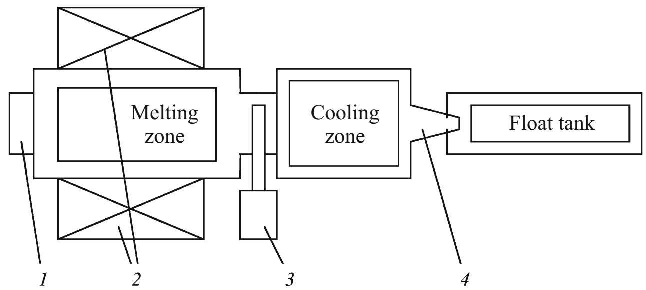

Fig. 1. General schematic of a 600 tons/day regenerative glassmaking furnace for float-glass manufacture: *1*) doghouse; *2*) regenerators; *3*) mechanical mixer; *4*) pouring spout.

occurring during cooling from the fining to the extraction temperature. To answer this question it is necessary to take account of the fact that chemical uniformity of the glass presumes structural uniformity on the nano- and microlevels.

This analysis of the operation of industrial glassmaking furnaces with different capacity for the manufacture of sheet and container glass as well as glass fibers has shown that the residence time of the molten glass in the furnace depends little on its nominal capacity and is in the range 48 – 72 h.

It can be concluded on this basis that high-quality molten glass ready for extraction possesses completely definite nano- and microstructures as well the required extraction properties, viscosity and surface tension.

In turn, this presumes that the structure of the molten glass is optimal for sheet and container glasses and glass fiber as a function of the glass cooling time and temperature in the interval 1500 – 1150°C.

A simplified diagram of a 600 tons/day gas-air glassmaking furnace, which is part of float-glass production lines at the AGC Flat Glass Europe Company, is presented in Fig. 1. The chemical composition of the glass is as follows (wt.%): SiO_2 — 72.0; Al_2O_3 — 0.64; CaO — 8.95; MgO — 4.39; Na_2O — 13.63; SO_3 — 0.29; Fe_2O_3 — 0.06; and, TiO_2 — 0.04. The temperature – time regime for glassmaking in this furnace is shown in Fig. 2.

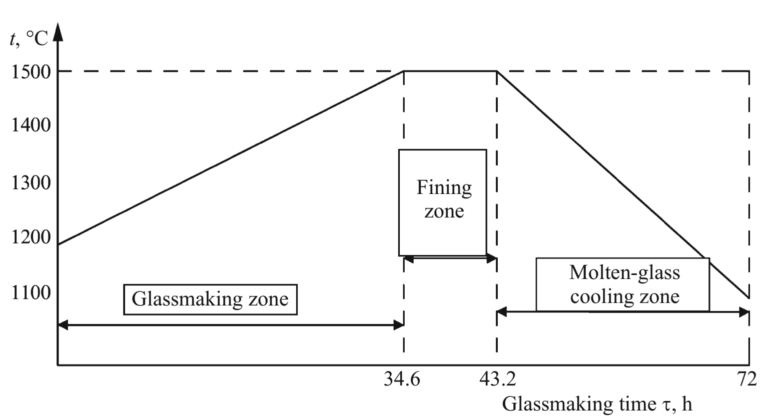

Fig. 2. Temperature – time glassmaking regime.

Technical Characteristics of a Glassmaking Furnace

Capacity, tons/day	600
Glass color	Colorless
Molten glass density, tons/m^3	2.5
Melting temperature, °C	1500
Total furnace area, m^2	600
Melting zone area, m^2	360
Cooling zone area, m^2	240
Molten glass in the furnace, tons	1800
Molten glass in the melting + fining zones, tons	1080
Molten glass in the cooling zone, tons	720
Molten glass residence time in furnace, h, including:	72.0
melting zone	34.6
fining zone	8.6
cooling zone	28.8
Average glassmaking rate before the fining zone, K/h	8.76
Glassmaking rate with fining zone, K/h	7
Molten glass cooling rate	12.1
Specific energy consumption, kJ/kg (kcal/kg)	4000 (956)

The batch quality number, spR × 10^6, for making float-glass is 4.2. This shows that the batch is of good quality and has high uniformity as well as good working characteristics.

The products of solid- and liquid-phase reactions and polymorphous transformations in the batch to 1200°C are Na_2SiO_3, $MgSiO_3$, β-$CaSiO_3$, $Na_4Ca_4(Si_6O_{18})$ and β-quartz. As temperature increases to 1400°C the chemical compounds formed decompose partially or completely as a result of thermal dissociation of ionic and ionic-covalent bonds ≡Si–O–Me, while the degree of polymerization of the silica decreases. The viscosity of the molten glass in the fining zone is 10 – 30 Pa · sec.

The main structural elements of the glass melt in this zone of a glassmaking furnace are dissociated ions of alkali and alkaline-earth metals and silicon-oxygen anions of different structural types ranging from orthosilicates $[SiO_4]^{4-}$ to chain and ring silicates $[SiO_4]_m^{n-}$. A conventional silica depolymerization (dissolution) diagram at this stage of glassmaking is shown in Fig. 3.

The high-temperature structure of glass melt in the fining zone can be characterized as chemically, temperature-wise, and structurally uniform base nanostructure, which includes free anions (radicals) of the melted silicates of alkali and alkaline-earth metals, anionic products of silica depolymerization and the cations Na^+, Ca^{2+} and Mg^{2+}.

The molten glass is prepared for forming by cooling at the average rate 12 K/h from the fining temperature to the temperature at which the glass is poured into the float tank; the cooling time is about 29 h. In this temperature interval, from 1500 to 1150°C, the initial anionic structure of the future glass is formed by reduction of the chemical bonds ≡Si–O–Si≡ with polymerization of the silicon-oxygen chain (a) and ring (b)

anions to 3- and 6-membered rings according to the following scheme:

a) chain: $[SiO_4]^{4-} \rightarrow [Si_2O_7]^{6-} \rightarrow [Si_3O_{10}]^{8-} \rightarrow [Si_6O_{19}]^{14-}$;

b) ring: $[Si_3O_{10}]^{8-} \rightarrow [Si_3O_9]^{6-} \rightarrow [Si_6O_{19}]^{14-}$.

As polymerization of silicon-oxygen anions proceeds and the anions grow in size the viscosity of the molten glass increases to 10^2 Pa · sec. Reduction of the ionic chemical bonds of the cations Na^+, Ca^{2+} and Mg^{2+} with the silicon-oxygen anions in the structure of the molten glass is unlikely to occur in this temperature interval, and the molten glass retains is fluidity.

The temperature – time cooling regime for the molten glass must secure a nanosize structure of the glass without risk of formation of anionic groupings of different size; the latter can degrade the chemical and structural uniformity of the molten glass, increase proneness to crystallization and decrease the extraction properties. The determining factor under these conditions is the thermal uniformity of the molten glass as its temperature in the cooling zone decreases at the rate 10 – 12 K/h. In modern glassmaking furnaces efficient cooling of the molten glass is achieved by increasing the surface area and decreasing the depth of the cooling zone. The optimal depth of the molten glass is 30 – 40 cm (12 – 15 inches) for tinted glasses [6, 7]. For colorless glasses the depth of this zone is 2 – 5 times greater.

The cooling conditions for the molten glass in container and float glass furnaces can be obtained by different methods, assuring nevertheless adequate chemical uniformity.

In the standard 200 – 400 tons/day glassmaking furnaces used for manufacturing container glass the cooling regime for the molten glass is optimized by means of the dam height, which, essentially, plays the role of a sliding throttle valve, which increases or decreases the cooling rate of the molten glass and, correspondingly, changes its residence time in the cooling zone.

The effect of the dam height on the chemical uniformity of container glass in 250 – 450 tons/day furnaces is presented in [7]. It is shown that a change of the dam height in the range 0.2 – 1.1 m produces an appreciable change of the quality of the ready glass and the extraction properties of the molten glass. It is recommended that the dam height be limited to 0.6 – 0.8 m in order to optimize the molten-glass flow in the melting and cooling zones of a glassmaking furnace. Although the time factor was neglected in the work the data obtained point to the optimal temperature – time regime for cooling the glass.

In the 400 tons/day L_0NO_x Melter furnaces, manufactured by the SORG Company, with a gas-air heating system the fining and cooling zones include shallow and deep zones and the molten glass is cooled in a vertical flow rather than a horizontal flow. However, the residence time of the molten glass in the cooling zone, including the extraction part of the furnace, is the same as that indicated by the analysis and equals about 22 h. Just as in the furnaces manufactured by the AGC Flat Glass Europe Company, the ratio of the residence time of the molten glass in the melting and cooling zones is approximately 2 : 1.

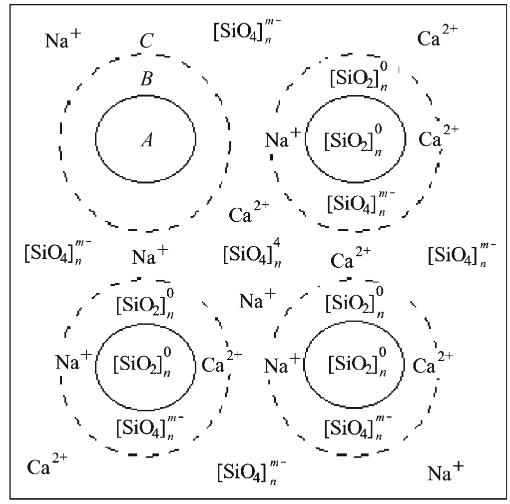

Fig. 3. Diagram of depolymerization of silica in melt of alkali silicates of sodium, calcium and magnesium in the fining zone: *A*) crystalline modifications of SiO_2; *B*) partially depolymerized layer on a silica surface; *C*) melt (alkali silicates).

The analysis of the glass melting process has shown that the glass melting time in modern glassmaking furnaces is 48 – 72 h and depends on the cullet content in the batch (60 – 70 wt.%), the completeness of the chemical reactions at the silicate-formation stage and the degree of depolymerization of the silica in the molten glass. The glass melt retains its chemical and structural uniformity with cooling rate 10 – 12 K/h and total cooling time 20 – 24 h.

To increase the melting rate of glass with cullet content in batch to 60 wt.% or more in large-tonnage glassmaking furnaces it is desirable to use new-generation catalysts for high-temperature chemical reactions in the system $Na_2O–MgO–CaO–SiO_2$.

The experimental data show that catalysts lower the temperature at which the chemical reactions occur in glass batches at a higher rate and, which is especially important, accelerates the depolymerization of the silica; catalysts also promote the formation of chemically and structurally uniform molten glass with silicon-oxygen chain anions predominating in its nanostructure. The stability of the properties and characteristic temperatures (T_g, T_f, T_L) of the ready glass is good. The glass melting time is about 20% shorter. The energy consumption on glass melting in batches with catalysts decrease by 10 – 15% from 4000 to 3500 kJ/kg (950 and 830 kcal/kg) as a result of a decrease of the melting time in the glassmaking furnace as compared with oxygen furnaces and L_0NO_x Melter furnaces, whose specific energy consumption ranges from 3650 to 3850 kJ/kg (870 and 920 kcal/kg), respectively.

Analysis of the operating conditions of glass furnaces has shown that the temperature – time regime for glass cool-

ing determines the chemical and structural uniformity of the molten glass. It was determined that the optimal cooling rate for the molten glass must not be less than 12 K/h with the total cooling time not exceeding 24 h. As the cooling rate increases, large silicon-oxygen ring anions, which can be presumably identified with the cristobalite structure and can surpass nanoscale dimensions, are less likely to form. The molten glass retains structural and chemical uniformity and high quality of the ready glass is secured.

Analysis of the material balance in industrial glass-making furnaces used to manufacture sheet and container glass comports with existing studies of the dependence of the chemical uniformity and quality of heat-polished glass on the furnace capacity [6] as well as with studies of mass-transfer processes in furnaces used to manufacture of sheet glass [7]. It has been determined that when the furnace capacity is increased from 400 to 500 tons/day the chemical uniformity and, correspondingly, the quality of glass increase. This can be explained by the increase of the cooling rate of the molten glass and decrease of the residence time of the molten glass in the cooling zone, where the anionic structure of the molten glass is formed. When the furnace capacity is increased from 420 to 380 tons/day cords appear and glass quality decreases. The glass melting time was evaluated from the emergence time of the indicator — cerium oxide, introduced with the batch into a 360 tons/day furnace. The maximum CeO_2 concentration in the glass ribbon was observed 58 – 76 h later. Using other data the CeO_2 emergence time was determined to be 2 – 4 days with a maximum on the third day [3].

The dependence of the chemical uniformity of the glass on the furnace capacity can be explained by an increase or decrease of the cooling rate of the molten glass and change of its residence time in the cooling zone from 1460 to 1150°C, during which the anionic structure of the glass is formed. As the cooling time increases the silicon-oxygen anions in the structure of the molten glass increase in size and their chemical uniformity degrades.

The total volume of the molten glass in the melting and cooling zones of the furnaces studied corresponds, on average, to their three-day capacity, while the cooling time with temperature reduction rate 12 – 15 K/h is 28 – 20 h. The rate of heating of the batch and molten glass in the melting zone of the glass furnace has little effect on the quality of the finished glass. Optimization of the temperature – time regime of the glass furnace and an increase of the temperature rise rate in the melting zone to 15 – 20 K/h make it possible to lower the energy consumption by 10 – 15%, decrease the amount of carbonic and nitrogen oxides discharged into the atmosphere, and increase the chemical uniformity and quality of the finished glass.

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